Dielectric Study of the sol gel transition of PNIPAM hybrid gels

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Abstract: As temperature increase, thermally sensitive spherical poly(N-isopropylacrylamide)(PNIPAM) microgels with a lower critical solution temperature (LCST) collapse into a individual microgel sphere. This process was monitored by analyzing dielectric spectrum over broad temperature. To examine the effect of PNIPAM concentration on the transition progress, dielectric measurements were carried out for the three systems, and electrical parameters of the microgel were calculated by Hanai's equation. The thermodynamics quantities associated with the collapsing process were obtained by using Eyring equation and relaxation parameters.

Keywords: PNIPAM microgels, Dielectric relaxation, Interface polarization, Orientation polarization, Entropy change.

1. Introduction

Nonergodic dynamics, rheological properties and dielectric properties for a novel thermally sensitive PNIPAM hybrid gel, have been studied by Chi Wu[1] and by many researchers[2], respectively. However, in these studies, the dielectric modes are usually considered to be caused by bound water and ion fluctuation, and other possible relaxation modes were rarely involved. Peculiarly, for PNIPAM system, the sol gel transition is accompanied the volume change of PNIPAM microgel with temperature, leading to a change in phase interface properties. Therefore, the relaxation process will be dominated by interface polarization mechanism. The motives of this study is to examine the causes of the volume-concentration induced sol-gel transition dynamic process below and above LCST and to understand the sensibility of dielectric spectroscopy method to the systems in which jamming phenomenon happens.

2. Experimental

The preparation of PNIPAM microgel can be found elsewhere[1]. The purified dispersion was diluted to three concentrations (*C*p) of 5.6 wt.%, 2.8 wt.% and 1.4 wt.%, respectively. The three solutions were measured with the circulating water pump controlling the temperature of the sample over a frequency range from 40 Hz to 110 MHz using 4294A Impedance Analyze.

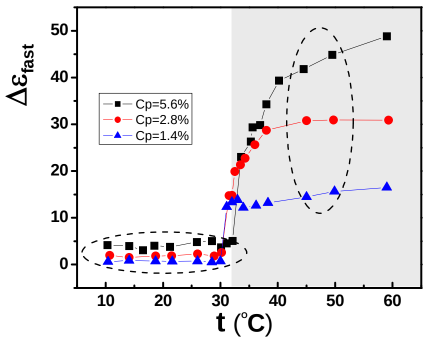

Figure 1. Temperature dependence of dielectric increment of fast relaxation for PNIPAM gel system with Cp=5.6%, 2.8% and 1.4%.

3. Results and discussion

Two relaxations, i.e. slow and fast relaxation for three solutions were observed. The fast relaxation is due to the fluctuation of counterions below LCST and to interfacial polarization above LCST. When temperature is below LCST, relaxation time τ_{fast} and dielectric increment $\Delta\varepsilon_{fast}$ hardly change with temperature, and τ_{fast} is independent of the concentration as well as temperature, while $\Delta\varepsilon_{fast}$ slightly increases from 2 to 5 with the rise of the concentration(Fig.1). This indicated that the relaxation mechanism will not change with the concentration below LCST. However, when above LCST, $\Delta\varepsilon_{fast}$ increases appreciably with rise of concentration(Fig.1), and the increase amplitude is proportional to the concentration. This is because PNIPAM microgels collapse into individual microgel sphere and leads to the interface polarization. The phase parameters, permittivity and conductivity of microgel and water, and the changes of water content in the microgel sphere with temperature were calculated by Hanai's equation. The results shows that above LCST, entropy change ΔS for three different concentrations are less than zero, showing the collapsing process happened.

4. Conclusions

By discussing the dependence of dielectric increment and relaxation time on temperature with the sol-gel transition model, mechanisms of two relaxations determined to be caused by fluctuation of counterions below the LCST and interfacial polarization above the LCST for fast relaxation. Based on the discussions about the temperature dependence of permittivity and conductivity for microgel (ε_p, κ_p) and the water content in PNIPAM gel ball, it can be concluded that the sol-gel transition process of PNIPAM microgel can be also detected by the dielectric method.

References

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